

SCIENCE FOR CERAMIC PRODUCTION

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PRODUCTION OF INTERIOR FACING TILES USING LOCAL RAW MATERIALS

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Mix compositions for interior facing tile have been developed using local raw materials: low-melting polymineral clay from the Gaidukovka deposit, dolomite from the Ruba deposit, granitoid dust from the Mikashevich deposit and sand from the quartz Gomel' Mining-Enrichment Works as well as DNPK refractory clay and KS-1 kaolin, both imported from Ukraine. The ceramic tiles have high physical-chemical properties.

Key words: facing tile, mechanical strength, water absorption, shrinkage, anortite, quartz, hematite.

The present study is concerned with developing for interior facing ceramic tiles mix compositions in the system clay raw material – granitoid dust – dolomite – quartz sand.

The use of local polymineral raw material can reduce production costs and conserve imported ceramic raw materials used in obtaining materials with the required operating properties.

In the course of these studies mix compositions in the raw-materials system chosen were developed and the physical-chemical properties of sample articles were studied in relation to the structure and phase composition.

The experimental composition region presented in Fig. 1 is bounded by the content of the components within the following limits (%³): clay raw material 59.5 – 72, granitoid dust 15.0 – 27.5 and Ruba dolomite 6.0 – 18.5. The content of quartz sand remained constant at 7%.

The following clay raw materials were used as the initial components: DNPK refractory clay (Ukraine), KS-1 kaolin (Ukraine) and low-melting polymineral clay from the Gaidukovka deposit (Minsk Oblast); class-4, grade-A, group-1 dolomite from the Ruba deposit (Vitebsk Oblast); granitoid dust from the Mikashevichi deposit (Brest Oblast); and, OVS-020-V grade quartz sand from the Gomel' Mining-Enrichment Works.

At all stages of development the production of facing ceramic is based on clay and other plastic materials (kaolin) as

the ideal product for obtaining a ceramic article. Aside from plasticity, which is required for molding ceramic tile, the reasons for using these raw materials are as follows: the clay reserves are large, the clay is inexpensive, ecological safety is assured, the kilning temperatures are relatively low, and the required degree of sintering and adequate mechanical strength of ceramic articles are secured. For this reason, clay raw material (low-melting, refractory clay and kaolin) forms the basis of the ceramic mixes.

Low-melting clay was introduced into the mix in order to impart to the mix the plasticity required for the subsequent molding operations.

Clay from the Gaidukovka deposit is characterized by the polymineral nature of its composition, the high content of free quartz (to 35 – 38%) and coloring oxides (5 – 8% Fe₂O₃ and TiO₂), and the presence of carbonate inclusions (to 7%).

The mineralogical composition of the clay is as follows (%): kaolinite 23 – 29, montmorillonite 10 – 15, hydromica 20 – 22, quartz 32 – 37, and impurities in the form of 4 – 6% carbonate inclusions. The chemical composition of the clay is as follows: 47.38 – 75.71 SiO₂, 8.45 – 11.86 Al₂O₃, 2.86 – 4.38 (Fe₂O₃ + FeO), 0.63 – 0.85 Na₂O, 2.95 – 4.66 K₂O, 2.16 – 4.78 MgO, 6.45 – 11.26 CaO, 0.56 – 0.68 TiO₂, and 8.57 – 14.1 other.

The use of refractory clays in pastes for obtaining facing tiles makes it possible to expand the sintering temperature range by 100°C, and this decreases the possibility of deformations arising during kilning. DNPK refractory clay is characterized by the following oxide content (%):

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³ Here and below, content by weight, %.

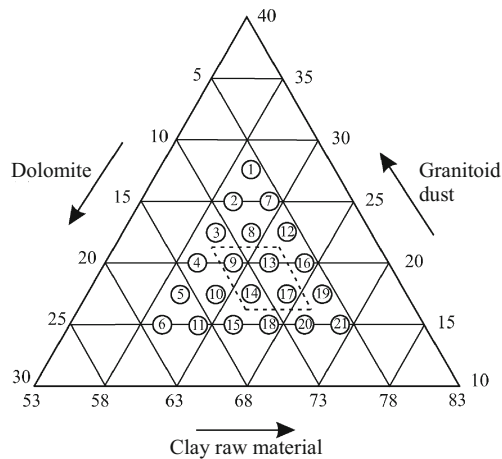


Fig. 1. Region of experimental compositions: the quartz sand content is constant at 7 wt.%; - - - -) region of optimal compositions.

57.2 – 67.6 SiO₂, 20.0 – 27.0 Al₂O₃, 1.45 – 1.80 (Fe₂O₃FeO), 1.2 – 2.5 (Na₂O + K₂O), 0.2 – 0.9 MgO, 0.3 – 0.95 CaO, 0.46 – 1.66 TiO₂, and 6.5 – 11.0 other [1].

Grade KS-1 kaolin with the following composition was introduced into the mix in order to regulate the rheological properties of the slip (%): 47.9 – 50.2 SiO₂, 36.8 – 38.5 Al₂O₃, 0.16 – 0.20 CaO, 0.07 – 0.10 MgO, 0.08 – 0.12, Na₂O, 0.050 – 0.67 K₂O, 0.49 – 0.55 Fe₂O₃, 0.060 – 0.93 TiO₂, and 10.0 – 12.9 other.

The quartz sand used as a nonplastic component contained the following (%): 97.3 – 98.8 SiO₂ and 0.04 – 0.15 Fe₂O₃.

Granitoid dust (Mikashевичi deposit) formed during the production of road stone was added in the following amounts as a nonplastic and partially fluxing component (%): 54.0 – 65.30 SiO₂, 0.62 – 0.89 TiO₂, 15.01 – 17.3 Al₂O₃, 5.37 – 8.61 (Fe₂O₃ + FeO), 2.09 – 3.23 MgO, 3.40 – 6.43 CaO, 3.41 – 3.98 Na₂O, 2.96 – 3.69 K₂O, and 1.29 – 2.60 other. The principal rock-forming granitoid minerals are plagioclase, microcline, quartz, and biotite; secondary minerals are epidote, chlorite, and sericite.

Dolomite in the mix acted as a fluxing agent and reduced the shrinkage of the ceramic tiles. The chemical composition of the dolomite is represented by the following oxides (%): 3.14 – 3.50 SiO₂, 0.69 – 1.20 Al₂O₃, 28.20 – 30.4 CaO, 18.9 – 20.0 MgO, 0.08 – 0.12 Na₂O, 0.26 – 0.35 K₂O, 0.37 – 0.45 Fe₂O₃, 0.03 – 0.08 TiO₂, and 36.5 – 46.12 other.

This combination of raw materials in the ceramic mix presupposed the possibility of regulating the sensitivity to drying and the degree of sintering of the material at the temperature of no-glaze (first-time) kilning (1110 ± 10)°C.

The ceramic mixes were prepared by the conventional slip technology with the compounds ground separately in a SPEEDY wet-grind ball mill (Italy) with milling-body to material ratio 1.3 : 1. The moisture content of the slip was 35 – 36%. To obtain the press powder the slip was dried at temperature no higher than 150°C and then comminuted

TABLE 1. Properties of Sample Ceramic Tiles in the Optimal Composition Region

Composi- tion No.	Mechanical bending strength, MPa	Water absorp- tion, %	Density kg/m ³	Porosity, %	CLTE, 10 ⁻⁷ K ⁻¹	Fire shrinkage, %
9	22.8	16.17	1.705	27.89	61.30	1.18
13	25.3	14.75	1.745	28.16	61.08	1.22
14	23.5	15.20	1.723	34.03	61.52	1.24
17	29.9	13.81	1.789	25.01	62.05	1.20

to the following sieve residues (%): No. 1 – 0–3, No. 05 – 10–25, No. 025 – 50–65, and total passage through sieve No. 025 – 20–35. The tiles were pressed in two stages in a laboratory press with specific pressing pressure (30 ± 2) MPa. The pressed tiles were trimmed along the lateral surfaces, dried at the maximum temperature (150 ± 10)°C, and then kilned in a SNOL 6.7/1300 laboratory electric furnace (Latvia) with soaking at the maximum temperature (1110 ± 10)°C for 20 min.

The quality of the articles obtained was evaluated according to a system of physical-chemical properties (density, porosity, fire shrinkage, water absorption, and linear thermal expansion coefficient (CLTE)). By studying these properties the optimal composition region characterized by high performance properties of the sample articles was determined.

The properties of samples with the optimal compositions are presented in Table 1.

Analysis of the data in Table 1 showed that the compositions 13 and 17 are characterized by the highest mechanical strength and low water absorption, which can be attributed to carbonates. These compositions lie on a line corresponding to 8.5% dolomite. As is well known, carbonates lower the mechanical strength, which in the absence of carbonates reaches values above 20 MPa. This is because less CO₂ is released when the mixes are decarbonized and, correspondingly, porosity decreases while density and mechanical strength increase [2].

The mechanical strength increases as the dolomite content decreases to 6% but the fire shrinkage increases to 2.8%.

Figure 2 show plots of the density, water absorption, shrinkage, and strength versus the dolomite content in the mixes.

The shrinkage decrease can be explained by the fact that high carbonate content secures the formation of silicates and aluminosilicates of calcium and magnesium while as porosity increases, density decreases and, correspondingly, water absorption increases [3].

The CLTE of all experimental sample ceramic tiles lies in the range (61.08 – 62.05) × 10⁻⁷ K⁻¹, which predetermines the binding strength between the future glaze coating and the ceramic base and increases the heat-tolerance of the articles.

An important factor affecting the properties of ready ceramic articles is the degree of sintering, which depends directly on the chemical and mineralogical composition of the raw material used in the mixes. Especially important are the composition and structure of the liquid phase, which lower the reaction temperature and accelerate sintering.

It was determined that ceramic mixes which contain together with the cations Na^+ and K^+ the cations Mg^{2+} and Ca^{2+} sinter best; therefore, it is recommended that complex fluxing agents, specifically, granitoid dusts and dolomite, be added into the mixes. The oxides indicated must be present in amounts not less than 10%, which gives more intense sintering and a wide kilning range.

The particle-size composition of the slip mass must be taken into account in order to secure the required structure for densely sintered material with high physical-chemical properties. Figure 3 displays the results of a study of the particle-size composition of slip for tiles to be used as facing on interior walls. Particle-size analysis was performed with a Fritsch (Germany) Analysette laser particle sizer.

Analysis of Fig. 3 showed that particles ranging in size from 0.1 to 0.50 μm comprise about 35%, 0.50 – 1 μm 20%, and 1 – 2 μm 45%.

This composition pertains to a continuous composition with fractions from 0.1 to 2.5 μm , which subsequently will give denser packing of the particles. The melt is formed mainly as a result of finely dispersed clayey matter, which is completely amorphized during heat treatment, as well as the formation of low-melting eutectics, which are comprised mainly of fluxing agents containing a considerable amount of K_2O , Na_2O , and Fe_2O_3 .

The formation of products of crystallization during sintering in the kilning process is of considerable importance. Minerals of needle-, prism-, or plate-shaped habitus predominate among them. During subsequent cooling these minerals are cemented by the glass phase and serve as a kind of micro-reinforcement which makes the material stronger.

The phase composition of the synthesized ceramic tile samples, which was determined using a Brüker diffractometer (Germany), is represented by quartz, anortite, and hematite and is virtually the same for all samples with compositions lying in the experimental region of the system, the only difference being the intensity of the diffraction peaks, i.e., the relative content of the phases, of which hematite and anortite have the greatest effect on the strength properties.

The formation of hematite in the form of isometric pseudomorphoses is observed at 900 – 1000°C. Hematite crystallizes in the form of opaque plates up to 10 μm long. Hematite platelets are distributed chaotically, but sometimes form radial-fibrous aggregates.

Anortite crystallizes in high-silica melt enriched with calcium oxide and alumina. Its formation is associated with reactions occurring between CaO (arising as a result of the decomposition of dolomite), meta-kaolin (formed during the

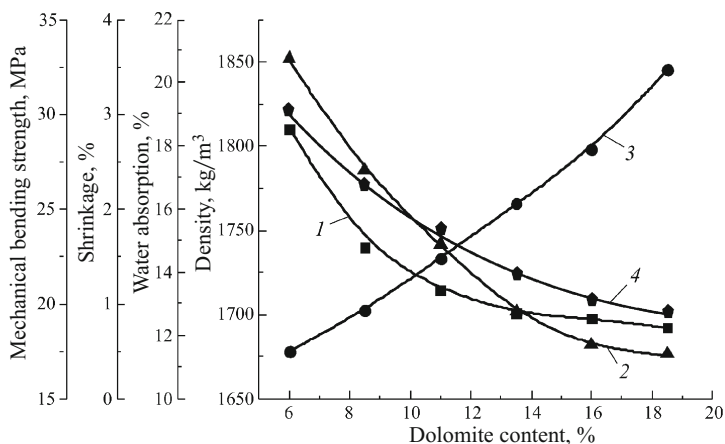


Fig. 2. Density (1), water absorption (2), shrinkage (3), and strength (4) of the ceramic versus the dolomite content.

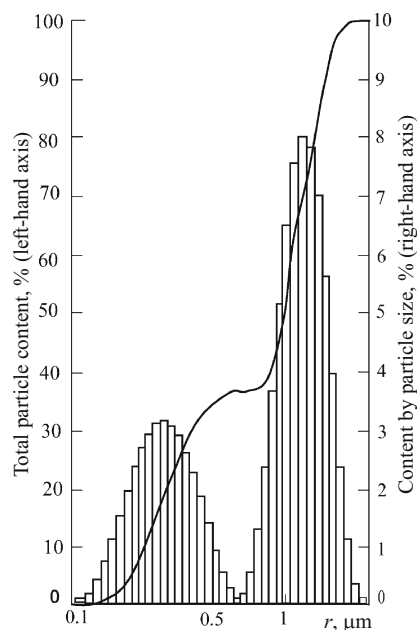


Fig. 3. Particle-size distribution of the disperse part of the slip.

kilning of clays), and quartz introduced together with the clays. The anortite crystals have the form of short thick prisms, less often needles or short prisms.

Thus, intense crystallization of prism- and plate-shaped crystals, which penetrate through the glass phase in different directions and thereby reinforce it, improves the strength and resistance to temperature differentials [2].

In the opinion of the authors of [3] one way heat tolerance and correspondingly the mechanical strength increase is by the dissipation of crack energy due to inclusions of non-isometric shape: needles, plates, and filamentary crystals. Such inclusions act on a crack tip by means of micro-fissuring, resulting in its reorientation and stress relaxation.

It should be noted that sample tiles obtained from optimal ceramic mixes are characterized by a large content of anortite, which could be one reason for the increase of the mechanical strength.

In summary, investigations have shown that it is possible to produce ceramic tiles, for use as interior facing of walls, with enhanced physical-chemical properties in the system granitoid dust – low-melting clay – dolomite – quartz sand.

The adoption of the compositions developed will lower the production costs of ceramic tiles as a result of the use of local raw materials — clays, dolomite, quartz sand, and granitoid dust — instead of imported materials.

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